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Investigation of the mass transfer processes during the desalination of water containing phenol and sodium chloride by electrodialysis

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A B S T R A C T

Oxidation processes are used in wastewater treatment when conventional processes are not effective due to the presence of recalcitrant organic contaminants, like phenol. However, the presence of ionic compounds associated with organic pollutants may retard the oxidation. In this work the transport of species contained in an aqueous solution of phenol containing sodium chloride was evaluated in an electrodialysis (ED) system. An experimental study was carried out in which the influence of the process variables on the phenol loss and sodium chloride removal was investigated. Experiments were also performed without current, in order to determine the phenol transfer due to diffusion. The phenol and salt concentration variations in the ED compartments were measured over time, using dedicated procedures and an experimental design to determine the global characteristic parameters. A phenomenological approach was used to relate the phenol, salt and water fluxes with the driving forces (concentration and electric potential gradients). Under ED conditions, two contributions were pointed out for the phenol transport, i.e. diffusion and convection, this latter coming from the water flux due to electroosmosis related to the migration of salts. The fitting of the parameters of the transport equations resulted in good agreement with the experimental results over the range of conditions investigated.

Keywords:

Electrodialysis
Desalination
Mass transfer
Wastewater
Phenol
Salt

1. Introduction

Since conventional wastewater treatment processes are hardly capable of removing biorecalcitrant organic pollutants, chemical oxidation processes are sometimes recommended. However, the presence of salts, like sodium chloride, together with the organic pollutants in industrial wastewaters, may inhibit or retard the degradation [1–3]. In such cases the wastewater desalination as a pretreatment process associated with the oxidation step can be attractive, for two reasons. Firstly, as explained before, organic pollutants are more easily oxidized in wastewater of low salt content. Secondly, the lower salt content in the treated water can improve the possibility to reuse it in the process itself or for other applications. Nevertheless, the interest to demineralise the wastewater before the oxidation is a consequence of balancing the additional costs due to the demineralization and the improvement of the separation efficiency that can be reached.

In the present work, the desalination by electrodialysis (ED) was considered. ED is an electrochemical separation process based on the selective transport of ions from one solution to another through ion-exchange membranes under the driving force of an electrochemical potential gradient. ED was mainly used to produce concentrated brines or salt depleted waters for industrial or domestic purposes, like to produce potable water from sea water for instance. But water desalination is not the only application. Stimulated by the development of ion-exchange membranes with better selectivity, lower electrical resistance, and improved thermal, chemical, and mechanical properties, other uses of ED, especially in food, drug, and chemical process industry as well as in biotechnology and wastewater treatment, have gained a broader interest [4].

In this paper, the desalination of a phenol saline solution, containing NaCl, by ED is investigated. On one hand, laboratory pilot scale experiments were carried out in order to evaluate the flow of the solvent and solutes through the membranes under different conditions. Based on the description of the solutes and solvent transfer involved in the system, an experimental strategy was developed to study the different transport contributions involved in the process. Experiments were also carried out using a diffusion cell and an ED system in order to determine the transport of the species through standard ion-exchange membranes (anion

Abbreviations: AEM, anion-exchange membrane; CEM, cation-exchange membrane; ED, electrodialysis; NaCl, sodium chloride; RO, reverse osmosis.

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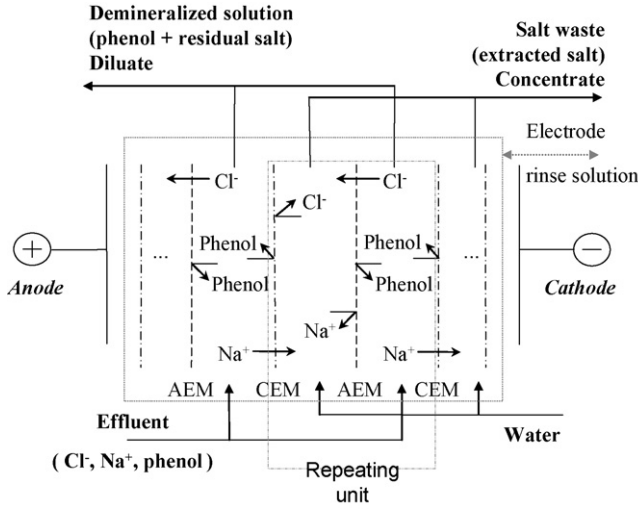


Fig. 1. Schematic representation of the demineralization of a saline solution containing phenol by ED; CEM: cation-exchange membrane; AEM: anion-exchange membrane.

and cation-exchange membranes) under different process conditions.

On the other hand, expressions coming from mass balance equations were used in order to describe the variation of the concentration of phenol and salt over time with respect to the operating conditions and solution composition. The characteristic parameters involved in these relationships were then determined by fitting the experimental results with the ones calculated by the model. These equations are an important tool in process design, since they enable to estimate the flow of the species present in the system as a function of process conditions. In this manner, it is possible to determine the efficiency of the process for the removal of NaCl from water contaminated with recalcitrant organic compounds like phenol, prior to its treatment by advanced oxidation processes, for instance.

2. System description

A schematic diagram for an ED stack is shown in Fig. 1 representing the desalination of a solution containing sodium chloride and phenol. It is composed of a number of identical cell pairs in parallel. Each cell pair consists of alternating cation-exchange membrane (CEM) and anion-exchange membranes (AEM), each one separated by a spacer through which the solutions flow. When an electric potential is applied across the stack, the cations in solution migrate towards the cathode. They can pass through the CEM, while they are stopped by the AEM. Meanwhile, anions migrate towards the anode. They can pass through the AEM but are stopped by the CEM. Consequently, the alternating compartments between consecutive membranes become increasingly enriched (concentrate), and depleted (diluate) in electrolyte.

2.1. Transport mechanisms

There are different contributions for the mass transfer of solution and solutes through the membranes in the ED stack.

Neutral as well as charged species can be transferred by diffusion caused by the chemical potential gradient between both sides of the membranes. The corresponding solute flux is directed towards the decreasing concentrations, i.e. from the more concentrated compartment to the more diluted one. The charged species are also transferred by migration caused by the electric current.

Normally the diffusion contribution is negligible compared to that of migration in most of the ED conditions.

The solvent flux through an ion-exchange membrane is the sum of two terms. The first one, known as the electroosmotic flux, is due to the shell of water molecules accompanying the migration of charged species under the influence of the electric current. The other one, the osmotic flux, is the solvent flux due to the chemical potential gradient of the solvent across the membrane [4]. Each of the two terms may be dominant depending on the permeability of the ion-exchange membrane, the concentration gradient, and the current density. Usually, under ED conditions, i.e. when an electric current is applied, the osmotic flux is negligible compared to the electroosmotic one.

Concerning neutral solutes, like phenol in this work, diffusion is the main contribution reported [5,6]. But from the theoretical point of view, a convective contribution can be expected for conditions such that the solution flow is significant.

2.2. Transport due to concentration differences

The flow of solution and solutes across a permeable membrane separating two well-mixed compartments can be described by Eqs. (1) and (2), proposed by Kedem–Katchalsky [7]. These equations are derived from irreversible thermodynamics and express the volumetric solvent flux, J_v ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$), and the solute fluxes, J_i ($\text{mol m}^{-2} \text{s}^{-1}$), across the membrane.

$$J_v = L_p(\Delta p - \sigma \Delta \Pi_i) \quad (1)$$

$$J_i = P_i \Delta \Pi_i + \bar{C}_i(1 - \sigma)J_v \quad (2)$$

where L_p is the membrane permeability to the solvent; Δp and $\Delta \Pi_i$ are the hydrostatic and the osmotic pressure gradients across the membrane, respectively; \bar{C}_i is the mean solute concentration on either side of the membrane, i and v refer to solute and solvent, respectively. The osmotic pressure gradient is scaled by the parameter P_i , the solute permeability coefficient, which is specific for each component i . σ is the reflection coefficient, which measures the relative restriction of the membrane to the solvent or solute flow. It varies from 0 for a freely permeable molecule to 1 for a non-permeating solute. In ED systems, the hydrostatic pressure term can be neglected compared to the osmotic pressure term [8]. In the case of water solutions, the water flux (J_w) can be considered as the result of the osmotic contribution only J_w^{os} . Then, when no current is applied, the water flux is expressed by the following equation:

$$J_w \cong J_w^{\text{os}} = L_p \sigma \Delta \Pi_i \quad (3)$$

Assuming dilute solutions, the Van't Hoff equation can be applied and the osmotic pressure gradient can be replaced by the difference of solute concentration across the membranes. Thus, in the present study, based on Eq. (2), the salt (J_s) and phenol (J_p) fluxes due to concentration differences can be expressed as Eqs. (4) and (5), respectively.

$$J_s = J_s^{\text{diff}} = P_s \Delta C_s \quad (4)$$

$$J_p = J_p^{\text{diff}} = P_p \Delta C_p \quad (5)$$

where superscript diff refers to diffusion contribution.

2.3. Transport under ED conditions

The fundamental aspects of ion transport under ED conditions are presented in a number of literature sources (for example, [4]). When a current is applied, the solvent flux is the result of two contributions, osmosis and electroosmosis J_w^{el} . The latter is proportional

to the current density applied, i , scaled by the water transport number, t_w , which relates the transport of water to the current, divided by F , the Faraday constant, as shown in the following equation:

$$J_w = J_w^{os} + J_w^{el} = L_p \sigma \Delta \Pi_i + \frac{t_w i}{F} \quad (6)$$

In normal ED conditions, i.e. when a current is applied, the osmosis contribution is negligible compared to that of electroosmosis. In practical applications, Eq. (6) can be written in a more simple form by using an electroosmotic coefficient α to relate the electroosmotic flux to the current density, as shown in the following equation:

$$J_w = J_w^{os} + J_w^{el} = L_p \sigma \Delta \Pi_i + \alpha i \quad (7)$$

A monovalent salt transfer rate can be expressed by Eq. (8), describing the diffusion, migration and convection contributions. The contribution of the migration to the salt transport can be expressed using the salt transference number, t_s , which is the fraction of the total current that is carried by the ions. In this case, it is expressed in moles of NaCl per mole of electrons, expressed in Faradays.

$$J_s = J_s^{diff} + J_s^{conv} + J_s^{mig} = P_s \Delta C_s + \frac{t_s i}{F} + \tilde{C}_s (1 - \sigma) J_w \quad (8)$$

Similarly to Eq. (7), the salt flux can be expressed as shown in Eq. (9), in which a coefficient β relates the amount of salt transported and the current density.

$$J_s = P_s \Delta C_s + \beta i + \tilde{C}_s (1 - \sigma) J_w \quad (9)$$

Usually, the migration contribution is preponderant over those of diffusion and convection, so that the first and third terms in Eq. (9) can be neglected with respect to the second one. The coefficients α and β are the sum of the contributions of the cation- and anion-exchange membranes. β express the quantity of salt transported per unit of electric charge applied, and can thus be considered as an efficiency term if the other terms in Eq. (9) are neglected.

The phenol transfer can be described by Eq. (10), following Eq. (2)

$$J_p = J_p^{diff} + J_p^{conv} = P_p \Delta C_p + \tilde{C}_p (1 - \sigma) J_w \quad (10)$$

The assumptions adopted in these equations can be verified by means of experimental results. Indeed, dedicated procedures can be used to evaluate the relative importance of the different phenomena that take place in the system. The parameters involved in the former equations can also be determined by fitting calculated and experimental values.

3. Experimental

The solutions were prepared by diluting phenol and/or sodium chloride (Acros Organics) in RO water with ca. $5 \mu S cm^{-1}$ conductivity to obtain the desired concentrations.

Two different equipments were used. On one hand, the phenol transport due to diffusion through the different ion-exchange membranes (AEM and CEM) was studied without current in a diffusion cell, the principle of which is depicted in Fig. 2. The system is composed of three fluid circuits: the one further called diluate is initially fed with the solution containing phenol and salt (0.5 L each). The two others, further called concentrate, were initially fed with reverse osmosis (RO) water. Because of the chemical potential difference, phenol and salt are carried through the membranes from the diluate to the concentrate. Consequently, the masses of both solutes decrease in the diluate while they increase in the concentrate circuits. Since these circuits are separated, the transfer through the AEM and CEM can be distinguished. Each membrane

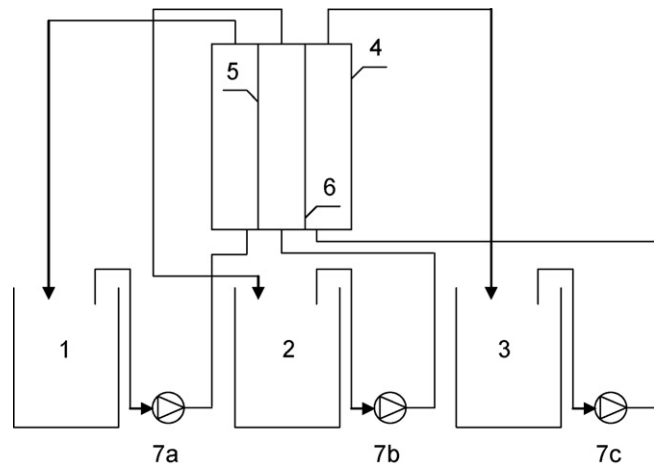


Fig. 2. Diffusion cell diagram. (1) Concentrate compartment of the CEM; (2) diluate compartment (feed); (3) concentrate compartment of the AEM; (4) diffusion cell; (5) CEM; (6) AEM; (7a-c) pumps.

has an effective area of $0.004 m^2$. Three centrifugal pumps were used to circulate these solutions.

The flow rate was set at a constant value of $4 L h^{-1}$ for all streams. A heat exchanger was used to maintain the temperature at $25 \pm 0.5 ^\circ C$. The experiments were carried out for a total time of 6 h. Samples of the solutions in the compartments were taken at different times and analyzed in order to monitor the phenol and salt concentrations over time.

On the other hand, ED experiments were performed with a EUR 2B-10 ED stack, supplied by Eurodia Industrie, equipped with AMX and CMX Neosepta membranes (Tokuyama Soda). The stack comprised 10 cells (AMX/CMX). For each type of membrane, the total active area was $0.2 m^2$, i.e. $0.02 m^2$ per cell.

The ED experiments were operated in batch mode (complete recycling of diluate and concentrate). The diluate compartment was initially fed with 2 L of different solutions containing phenol and salt, while the concentrate was fed with 2 L of RO water. The electrode compartments were fed with 3 L of a sodium chloride solution at a concentration of $9 kg m^{-3}$. The pH of the solution remained at ca. 7 in all experiments. Under this condition, the behavior of phenol is not expected to change from its neutral form. The feed flow rates were set at constant values of $180 L h^{-1}$ for the diluate and concentrate, and $360 L h^{-1}$ for the electrode solution. A heat exchanger was used to keep the temperature of the fluids at $25 \pm 2 ^\circ C$. In order to minimize the transient time, circulation of the solutions was started 1 h before the current was applied, so that the membranes could be properly soaked with the solution. After this time, the electric current was set at the desired level, and time measurement was started, with periodic sampling of solutions.

In the ED experiments, solution conductivities, temperature, electric current and voltage were measured in real-time. Conductivity was measured with a HI933100 conductimeter (Hanna Instruments). The volume variation was monitored in the two compartments as a function of time. The experiment duration was determined according to the conductivity of the diluate. The experiments were stopped as soon as this conductivity reached ca. $5 mS cm^{-1}$. Consequently, different experiment times resulted, depending on the operating conditions.

The phenol concentration was determined by the total organic carbon concentration (TOC) (Shimadzu TOC-Analyser 5050A) and high-performance liquid chromatography (HPLC) analysis (Hypersil Hypercarb 7μ column, $100 mm \times 4.6 mm$, eluted with water-methanol 80:20, v/v, flow rate $0.5 mL min^{-1}$; detector UV

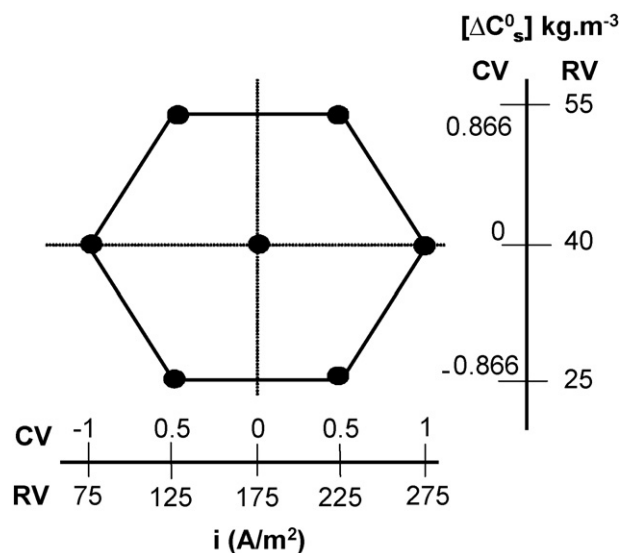


Fig. 3. Schematic representation of the Doehlert matrix for two variables, initial NaCl concentration difference between compartments, and current intensity; CV: coded variables; RV: real variables.

Waters 2487 at 270 nm; pump P600 Waters). The NaCl concentration was determined by conductivity. For selected samples, it was checked by performing ion chromatography analyses. The ion chromatograph comprised a Dionex system (IEC) with GP40 pump, CD20 conductivity detector, temperature of 30 °C; anions analysis: Ionpac AS11 column, AG11 guard column; ASRS-ultra at 300 mA suppressor; NaOH 5 mM and 1 mL min⁻¹ as eluent; cations analysis: Ionpac CS12A column, CG12A guard column, CSRS-Ultra at 100 mA suppressor, methanesulphonic acid (MSA) at 200 mM and 1 mL min⁻¹ as eluent.

A first set of experiments was performed with electric current set to zero, in order to assess the contribution of diffusion to the salt and phenol transfer, and osmosis to the solution transfer. In these experiments, the concentrations of salt and phenol in the diluate ranged from 0 to 55 kg m⁻³ and from 100 to 400 ppm C, respectively.

A second set of experiments was carried out under normal ED conditions at different current densities. An experimental design based on the Doehlert model [9] with two variables was used to study the effect of the current density and the initial salt concentration difference between the compartments, i.e. the initial NaCl concentration of the effluent. Fig. 3 represents the experimental domain explored. The range adopted for the initial NaCl concentration is representative of that in saline phenolic wastewaters. The limiting current, which is the maximum value that can be used, was determined as suggested by Cowan and Brown [10]. Experiments were then carried out at a constant current, in a range between 1.5 and 5.5 A, i.e. at current densities between 75 and 275 A m⁻². The

diluate was fed with a solution containing phenol at a concentration of 100 ppm C. A few experiments were also carried out with higher initial phenol concentrations, up to 400 ppm C. The results were evaluated following the variations of the liquid volume, and those of the quantities of phenol and NaCl in the compartments versus time.

For an easier data treatment and analysis, coded values were adopted for the variables. The responses were used in the least squares fitting of an empirical model based on the factors.

4. Experimental results and parameters fitting

4.1. Factor effects

For all the experiments, the amounts of solute and solvent transported were evaluated by measuring the changes in concentration and volume in the compartments with time. As a result, the water, salt and phenol fluxes, J_w (m s⁻¹), J_s (kg s⁻¹ m⁻²) and J_p (kg s⁻¹ m⁻²), were obtained from the rates of change of the volume, NaCl mass and phenol mass in the compartments, respectively, for different experimental conditions, as presented in Table 1, and using 100 ppm C (0.13 kg m⁻³) of phenol initial concentration in the diluate. The total active membrane areas considered were 0.2 m², S_1 , for the salt transfer, and 0.4 m², S_2 , for the water and phenol transfer and the fluxes (J) were obtained as indicated in Eq. (11) from the volumetric or mass flow rates (j).

$$J = \frac{j}{S} \quad (11)$$

The response surface methodology was used to evaluate the relationships between the controlled experimental factors (ΔC_s^0 and i) and the observed results (J_w , J_s , J_p). Equations of the following form (12) were fit to each response, y , as a function of the two factors, X_1 and X_2 .

$$y = aX_1 + bX_2 + cX_1X_2 \quad (12)$$

With empirical coefficients a , b and c estimated by least squares. The coefficients related to the factor contributions for the solvent and solutes fluxes are represented in Fig. 4 as a Pareto diagram showing the factors in terms of their relative contribution to each response.

The results show that the initial salt concentration difference (ΔC_s^0) between the compartments as well as its interaction with the current density (i) has negligible effect compared to that of the current density, especially for the salt flux, J_s . On the other hand, in the experiments where the current is set to zero, the presence of NaCl has no significant influence on the phenol mass transport due to diffusion.

In these experiments, the maximum deviation observed for the mass balance was 2.4%.

Table 1
Summary of the Doehlert matrix-based ED experiments for measuring water, NaCl and phenol fluxes

Experiment	Doehlert variables		Coded variables		Real variables		Responses		
	i X_1	ΔC_s^0 X_2	i X'_1	ΔC_s^0 X'_2	i (A m ⁻²) U_1	ΔC_s^0 (kg m ⁻³) U_2	J_w ($\times 10^{-7}$ m s ⁻¹) Y_1	J_s ($\times 10^{-5}$ kg m ⁻² s ⁻¹) Y_2	J_p ($\times 10^{-8}$ kg m ⁻² s ⁻¹) Y_3
1	0	0	0	-0.453	175	32.2	1.78	9.60	1.87
2	1	0	1	0.043	275	40.8	2.78	15.06	2.56
2'	1	0	1	-0.416	275	32.8	2.92	15.13	2.39
3	0.5	-0.866	0.5	-1.030	225	22.2	2.36	12.78	2.21
4	0.5	0.866	0.5	0.441	225	47.6	2.33	13.58	2.25
5	-0.5	0.866	-0.5	0.577	125	50.0	1.31	7.64	1.66
6	-1	0	-1	-0.176	75	37.0	0.78	4.61	1.28
7	0.5	-0.866	-0.5	-0.850	125	25.3	1.27	7.67	1.65

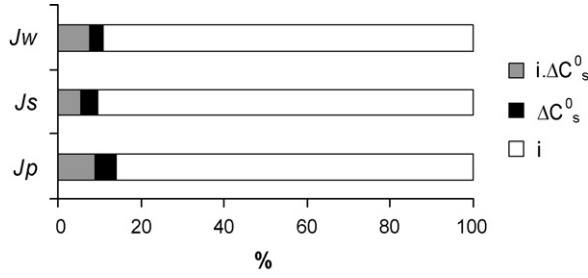


Fig. 4. Normalized Pareto diagram for the fluxes contributions.

The results are discussed in more details in the following sections.

4.2. Water and salt transport

The solvent and solutes transport were analyzed from the set of experiments carried out without and with an electric current. Since the initial salt concentration was found to be a negligible factor in the range studied, relationships were established between the different fluxes and the current density.

Fig. 5 shows the volume of solution in the concentrate compartment, i.e. that initially containing RO water, over time for different current conditions. As expected, the water flow has opposite directions for operation with and without current. On one hand, the volume decreases in the absence of electric current due to osmosis, that takes places in the direction of the increasing concentrations. On the other hand, when an electric current is applied, the solvent flow, which is mainly due to electroosmosis coming from the water carried by the migrating salt, is oriented in the same direction as the salt flux, i.e. from the diluate to the concentrate. Consequently, the volume in the concentrate increases. This major contribution of electroosmosis to water transport confirms previous observations in the literature [11]. In addition, when a current is applied, the volume varies linearly with time, indicating that the water flux is constant. Finally, the water flux increases with the current.

Concerning the salt transport, Fig. 6 shows the variation of the mass of salt in the concentrate over time for different values of the current density. One can observe that the diffusion contribution, i.e. that obtained for $i=0$, is very low compared to that coming from migration whatever the current density. Moreover, since the variation is linear, the salt mass flux can be considered constant with a good approximation.

The experimental results show that under ED conditions, i.e. when an electric current is applied, the water and salt fluxes can be considered as dependent on the current intensity only. They can be correlated to the current density by a linear regression, as pre-

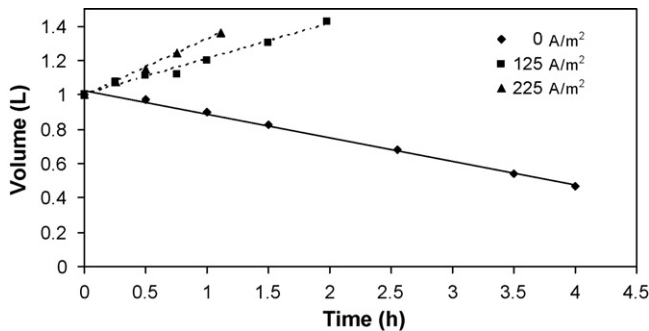


Fig. 5. Variation of the concentrate compartment volume over time for different current density values; [$\Delta C_s^0 \approx 55 \text{ kg m}^{-3}$; $\Delta C^0 = 100 \text{ ppm C}$].

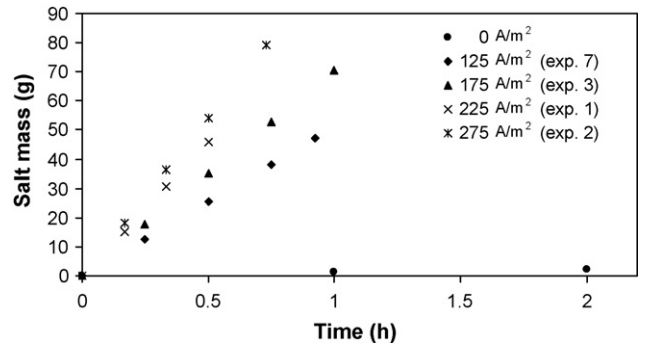


Fig. 6. Variation of NaCl mass in the concentrate compartment over time for different values of the current density.

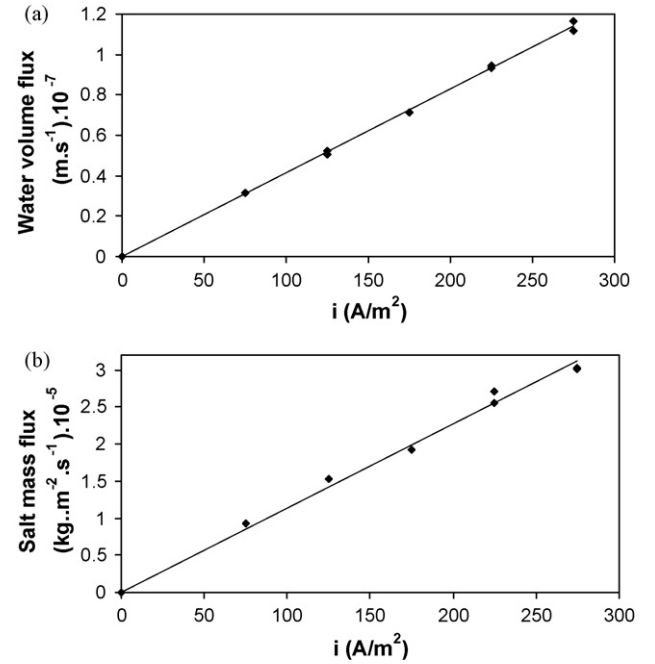


Fig. 7. Variation of the water (a) and salt (b) fluxes versus the current density.

sented in Fig. 7(a) and (b), with coefficients of determination equal to 0.998 and 0.990, respectively, considering no flux when no current is applied. This means that the contribution of diffusion to the salt flux as well as that of osmosis to the water flux are negligible. Then, for the conditions investigated in this study Eqs. (13) and (14) are valid. These equations are obtained from Eqs. (7) and (9), by neglecting the transport terms related to diffusion, convection and osmosis. This simplification is based on the experimental results shown in Figs. 5 and 6.

$$J_w = \alpha i \quad (13)$$

$$J_s = \beta i \quad (14)$$

with α equal to $(1.04 \pm 0.02) \times 10^{-9} \text{ m}^3 \text{ s}^{-1} \text{ A}^{-1}$ and β equal to $(5.5 \pm 0.5) \times 10^{-7} \text{ kg s}^{-1} \text{ A}^{-1}$. From the β coefficient the current efficiency using the Faraday constant can be estimated as 95%.

¹ 95% confidence interval.

Table 2

Operating conditions (current density and phenol concentration) and results (phenol flux) of the experiments carried out for evaluating the different contributions to the phenol transport

Experiments	i (A m ⁻²)	ΔC_p^0 (ppm C)	ΔC_s^0 (kg m ⁻³)	J_p ($\times 10^{-8}$ kg m ⁻² s ⁻¹)
Diffusion	0	359	0	3.86
	0	306	0	3.20
	0	231	0	2.43
	0	140	0	1.63
	0	87	0	0.95
	0	81	0	0.93
	0	73	0	0.85
	0	71	0	0.65
Additional	175	256	35	8.21
	275	256	35	9.64

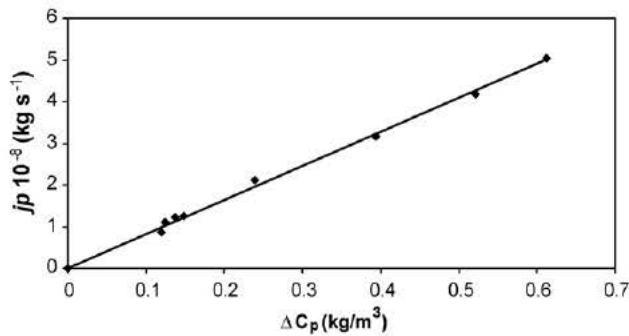


Fig. 8. Phenol mass flux versus concentration difference between compartments for $i=0$. Experiments without current (conditions in Table 2).

4.3. Phenol transport

The contributions to the phenol transport, as expressed in Eq. (10), were evaluated by means of experiments carried out under the conditions listed in Table 2.

The variation of the phenol flux versus the concentration difference is shown in Fig. 8 for solutions containing phenol without NaCl. One can state that this variation is linear. Then, according to Eq. (10), the phenol permeability coefficient P_p can be estimated from the corresponding slope. It is found equal to 8.4×10^{-8} m s⁻¹, with a coefficient of determination equal to 0.997.

The effect of the presence of salt on the diffusion contribution to the phenol transport was also investigated. Phenol mass over time for different salt concentrations is shown in Fig. 9. For the two phenol concentrations investigated, the initial NaCl concentration has no significant effect on the phenol flux. Then, the value of

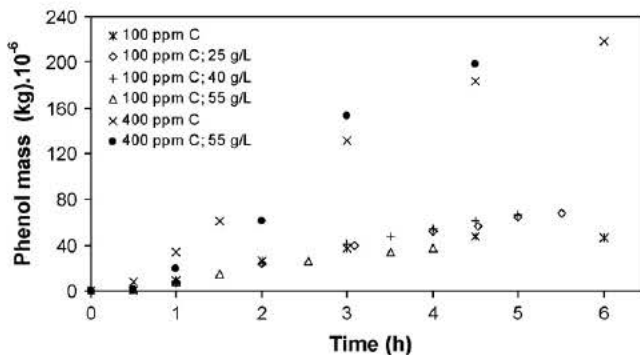


Fig. 9. Variation of the phenol mass in the concentrate compartment with time – influence of the initial concentrations of salt and phenol – experiments without current.

the phenol permeability coefficient determined with phenol solutions is valid for the whole range of phenol and salt concentrations investigated.

On the other hand, Fig. 10 shows the phenol mass in the concentrate compartment over time under ED conditions, i.e. with a current density. It is observed that, although phenol is not ionic, its transfer is affected by the current. Indeed, the phenol flux increases when the current density increases. For $i=275$ A m⁻² it is approximately 2.5 times that for $i=0$. Therefore, a convective contribution for the phenol transport is pointed out.

As described by Eq. (10), the resulting flux is directly related to the water flux. This latter depends, as previously discussed, on the electric current density applied, and the restriction of the membrane to phenol flow. In the experiments, the concentration difference between the compartments varied less than 15%, which is a relatively small value compared to the changes in the other variables. Then assuming that the concentration difference is approximately constant, the phenol transport due to diffusion can be considered approximately constant over time. This assumption was subsequently validated based on the good agreement obtained by fitting the experimental results of phenol flux versus time without current by a linear model. In the same manner, the initial concentration of phenol in the feed $C_{p,d}^0$, can be considered approximately equal to the phenol concentration difference between the compartments, ΔC_p^0 . Indeed, the experiments show that the concentrations in the two compartments remain close to their initial values. Based on these assumptions the phenol flux under ED conditions can be expressed as shown in the following equation:

$$J_p = P_p \Delta C_p^0 + (1 - \sigma) C_{p,d}^0 J_w \quad (15)$$

Thus, by fitting the experimental values of the phenol flux, J_p (kg m⁻² s⁻¹), to ΔC_p^0 and $(C_{p,d}^0 J_w)$ by a linear model, the value of the reflection coefficient, σ , can be estimated. A value of 0.24 ± 0.02 (see footnote 1) was obtained for the conditions tested, which means that the membrane retains approximately 24% of the phenol transported towards it due to convection. The parameter P_p was estimated as equal to $(8.4 \pm 0.8) \times 10^{-8}$ m s⁻¹. This value is identical to that obtained by fitting the experimental results obtained in the experiments carried out without electric current. Then, the formalism of Eq. (15), assuming that the phenol flux is the addition of a diffusion and a convention contribution is validated. Moreover, the linear model resulted in good agreement with the experimental results ($R^2=0.995$), as presented in Fig. 11, which shows experimental versus predicted results calculated by Eq. (15). The linear model expressed as Eq. (15) is able to correlate the phenol mass flux with its initial concentration difference between compartments and the water flow rate, which is proportional to the current intensity.

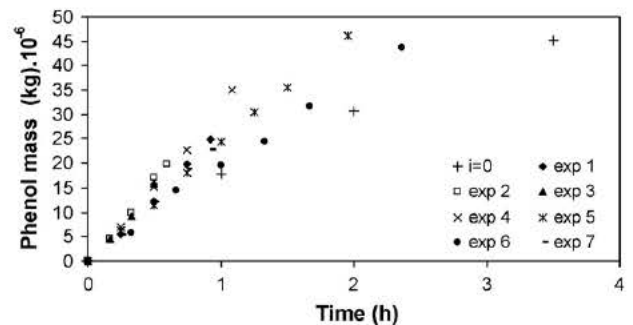


Fig. 10. Phenol mass in the concentrate compartment over time – influence of the current – $\Delta C_p^0 \approx 100$ ppm C.

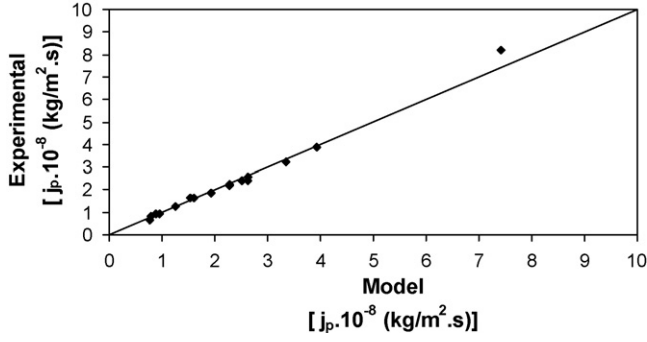


Fig. 11. Experimental versus predicted values for the phenol flux.

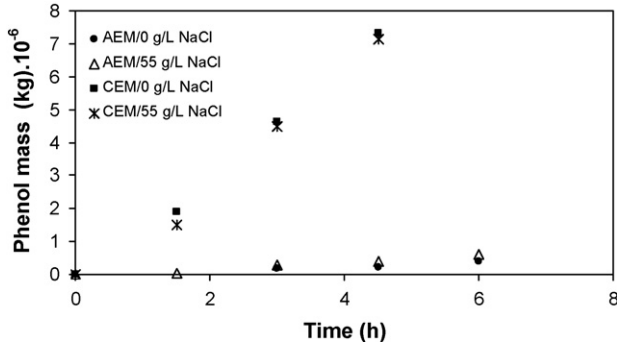


Fig. 12. Phenol mass variation over time through the CEM and AEM membranes, in water solutions with and without NaCl addition [$\Delta C_p^0 = 400$ ppm C, $I = 0$].

4.4. Phenol transport through the CEM and AEM membranes

A few experiments were also carried out in the diffusion cell in which the transport through the CEM and AEM can be evaluated separately. Fig. 12 shows the variation of the phenol mass transported through both membranes over time. The results show that the phenol transport through the CEM is significantly more important than that through the AEM. Under the conditions studied, the addition of salt does not seem to have an influence on the phenol flux through the membranes. The observed difference in phenol flow rate between both membranes may be dependent on the structure of the membranes. An investigation on this aspect was out of the scope of this work, and deserves further studies.

4.5. ED demineralization process performance estimation

Based on the experiments, the parameters of Eqs. (13)–(15) were estimated by a least-squares method. These parameters are specific for each solution and ED system studied, and their values have to be estimated using the methodology presented in the former sections. For the system investigated in this study, the values of these parameters are summarized in Table 3.

The variations of the salt and phenol concentrations in the compartments during the ED demineralization process can thus be

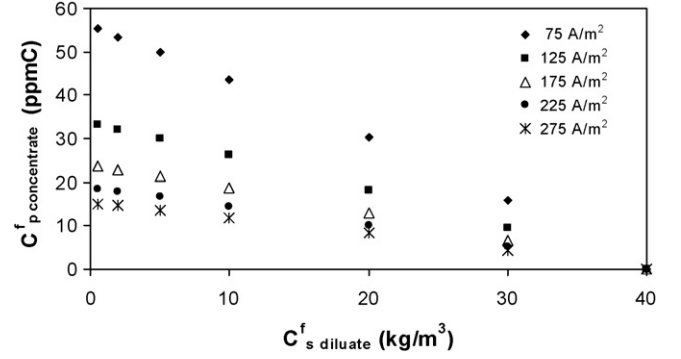


Fig. 13. Phenol final concentration in the concentrate compartment versus final NaCl concentration in the diluate compartment for different current density [$\Delta C_p^0 = 100$ ppm C; $\Delta C_s^0 = 40$ g/L].

obtained based on the mass balance equations in each compartment. For the concentrate compartment, and assuming constant salt mass flow rate, j_s , Eq. (16) gives the salt concentration C_s^t as a function of time t

$$C_s^t = \frac{j_s t + C_s^0 V_c^0}{V_c^t} \quad (16)$$

where V_c^0 is the initial volume and V_c^t is the volume in the concentrate compartment at time t . Considering that the water volume increase rate was found to be constant (linear variation of the volume versus time) and by taking into account the transport coefficients α and β (Eqs. (13) and (14)) and the membrane areas S_1 and S_2 , Eq. (16) results in Eq. (17).

$$C_s^t = \frac{\beta i S_2 t + C_s^0 V_c^0}{\alpha i S_1 t + V_c^0} \quad (17)$$

Based on the same assumptions, the phenol concentration can be expressed by the following relationship:

$$C_p^t = \frac{(P_p \Delta C_p^0 + (1 - \sigma) C_{p,d}^0 \alpha i S_1) t + C_p^0 V_c^0}{\alpha i S_1 t + V_c^0} \quad (18)$$

For the diluate compartment, similar equations can be written, resulting in Eqs. (19) and (20) for the salt and phenol concentrations, respectively, where V_d^0 is the initial volume in the diluate compartment.

$$C_s^t = \frac{(-\beta i S_2 t) + C_s^0 V_d^0}{(-\alpha i S_1 t) + V_d^0} \quad (19)$$

$$C_p^t = \frac{(-(P_p \Delta C_p^0 + (1 - \sigma) C_{p,d}^0 \alpha i S_1) t) + C_p^0 V_d^0}{(-\alpha i S_1 t) + V_d^0} \quad (20)$$

The experimental and calculated variations of the phenol and salt concentrations were compared, considering the values of the parameters provided in Table 3. The maximum difference between both values was less than 10% for the whole range of conditions investigated.

On the other hand, Fig. 13 shows an example of calculated results dealing with the demineralization of a phenolic solution containing

Table 3
Overall transport coefficients obtained in the experiments with the ED system

Water transport, α ($\times 10^{-9}$ m ³ s ⁻¹ A ⁻¹)	Salt transport, β ($\times 10^{-7}$ kg s ⁻¹ A ⁻¹)	Phenol transport	
		P_p ($\times 10^{-7}$ m s ⁻¹)	σ
1.04 ± 0.02^a $S_1 = 0.4$ m ²	5.5 ± 0.5^a $S_2 = 0.2$ m ²	8.4 ± 0.8^a $S_1 = 0.4$ m ²	0.24 ± 0.02^a

^a 95% confidence interval; S membrane transfer area.

NaCl. The variation of the phenol concentration in the concentrate compartment, corresponding to the phenol loss due to its transport to the concentrate, is plotted *versus* the salt concentration in the diluate compartment, i.e. the residual salt content in the demineralized phenolic effluent for different values of the current density.

As expected, for a given value of the current density, higher demineralization, i.e. lower salt concentrations, correspond to higher phenol loss. Indeed, higher demineralization means higher water flow and so higher phenol transport due to convection. One can observe also that the variation of the phenol loss *versus* the salt remaining content is more pronounced for the lowest current densities.

On the other hand, for a given salt concentration, i.e. a given demineralization, the phenol loss decreases as the current increases.

5. Conclusions

In this work, the transport of species contained in an aqueous solution of phenol and sodium chloride during ED was evaluated. An experimental study was carried out with aqueous solutions containing different amounts of phenol and NaCl and different operating conditions in order to quantify the different contributions to the water, phenol and salt transfer in the system. Concerning the water transfer, the contribution of electrosmosis was found to be predominant over that of osmosis as far as a current is applied. In the same manner, for the salts, the transfer due to migration was found predominant compared to that due to diffusion. Then, the current intensity can be considered as the most significant variable affecting water and salt transfer in the ED system.

On the other hand, concerning phenol, which is a neutral solute, a convective contribution due to the water flow was pointed out in addition to the expected contribution coming from diffusion. This later was found to be independent of the salt concentration. Whilst the contributions of diffusion and convection to the phenol transfer depend on the operating conditions, it was found that convection is significant in the range of current density normally used in ED.

For the conditions of this study, i.e. for the solutes and membranes used, the characteristic parameters of the equations relating the different contributions to the mass transfer were also determined. This was done by fitting experimental results with the ones calculated by the model. Mass balance equations were proposed to describe the evolution of the volumes and the salt and phenol concentrations in each compartment as a function of their initial values and of the current density. These equations depend basically on the transport parameters that have to be estimated experimentally for each membrane system.

Then, the ED performances, i.e. the loss of phenol and the salt concentration in the demineralized wastewater, can be calculated as a function of the operating parameters, like the current density or the initial salt concentration in the feed.

Finally, the experiments carried out in the diffusion cell enabled to quantitatively evaluate the transfer of phenol through the membranes. This information is important for the selection of membranes, since phenol loss should be kept as low as possible in effluent treatment processes comprising previous desalination by ED.

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Nomenclature

C	concentration (kg m^{-3})
\bar{C}	mean solute concentration on either side of the membrane (kg m^{-3})
F	Faraday constant ($96485 \text{ A s equiv.}^{-1}$)
i	current density (A m^{-2})
I	current intensity (A)
j	mass flow rate (kg s^{-1})
J	molar flux ($\text{mol m}^{-2} \text{ s}^{-1}$)
J_i	solute flux density ($\text{kg m}^{-2} \text{ s}^{-1}$)
J_p	phenol flux ($\text{kg m}^{-2} \text{ s}^{-1}$)
J_v	volumetric solvent flux density ($\text{m}^3 \text{ m}^{-2} \text{ s}^{-1}$)
J_w	water flux (m s^{-1})
L_p	membrane permeability ($\text{m s}^{-1} \text{ bar}^{-1}$)
m	mass (kg)
P_i	permeability coefficient ($\text{kg m}^{-2} \text{ s}^{-1} \text{ bar}^{-1}$)
P_p	phenol permeability coefficient (m s^{-1})
P_s	salt permeability coefficient (m s^{-1})
S	total active membrane area (m^2)
t	time (s)
t	transport number
V	volume (m^3)

Greek symbols

α	electroosmotic coefficient ($\text{m}^3 \text{ s}^{-1} \text{ A}^{-1}$)
β	current coefficient ($\text{kg s}^{-1} \text{ A}^{-1}$)
ΔC_p	phenol concentration difference between compartments (kg m^{-3})
ΔC_s	salt concentration difference between compartments (kg m^{-3})
Δp	hydrostatic pressure gradient between compartments (bar)
$\Delta \Pi$	osmotic pressure difference (bar)
σ	reflection coefficient

Subscripts

c	concentrate compartment
d	diluate compartment
i	solute i
n	neutral solute
p	phenol
s	salt
w	water

Superscripts

conv	convection
diff	diffusion
el	electroosmosis
os	osmosis

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